

# Quenching of Lamellar Ordering in an n-Alkane Embedded in Nanopores

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**Abstract.** – We present an x-ray diffraction study of the normal alkane nonadecane  $C_{19}H_{40}$  embedded in nanoporous Vycor glass. The confined molecular crystal accomplishes a close-packed structure by alignment of the rod-like molecules parallel to the pore axis while sacrificing one basic ordering principle known from the bulk state, i.e. the lamellar ordering of the molecules. Despite this disorder the phase transitions observed in the confined solid mimic the phase behavior of the 3D unconfined crystal, though enriched by the appearance of a true rotator phase known only from longer alkane chains.

The goal of manipulating matter on the nanometer scale has led to a particularly rich area of research on how basic concepts of condensed matter physics, i.e. geometric ordering principles like close-packing, phase transition phenomenology and thermodynamics are changed once one reaches this length scale. In fact, there has already been a tremendous increase in understanding of such phenomena by experimental [1] and theoretical [2] studies of fluids in nanoporous glasses. These randomly interconnected porous networks are unique systems in that they allow us to easily prepare and study systems in restricted geometry. It has been known for a long time that the freezing point of liquids is reduced and that the "capillary" condensation of the vapor occurs at a reduced vapor pressure in such geometries [1]. Little however is known of the impact of confinement on the solid state of matter. The few pore solids investigated so far had globular building blocks, significantly smaller than the mean pore diameter of the porous networks. They show structures closely related to the bulk state. Prominent examples are krypton, argon, nitrogen, oxygen and  $H_2O$  [3, 4, 5, 6].

In this Letter, we focus on the structure and phase transitions of a more complex molecular crystal, built of chain-like molecules whose lengths are comparable to the mean diameter of the pores. Our temperature dependent x-ray study elucidates how these confined molecules establish one of the basic building principles of condensed matter, i.e. close packing, despite drastic geometric restrictions in the pores. Furthermore, an analysis of the temperature dependent lattice parameters reveals that the confined alkane mimics order-disorder transitions known from the three-dimensional (3D) unconfined crystals.

For our x-ray powder diffraction study, we have chosen the n-alkane  $C_{19}H_{40}$  embedded in Vycor glass. From a transmission electron microscope photograph [7], Vycor can be described

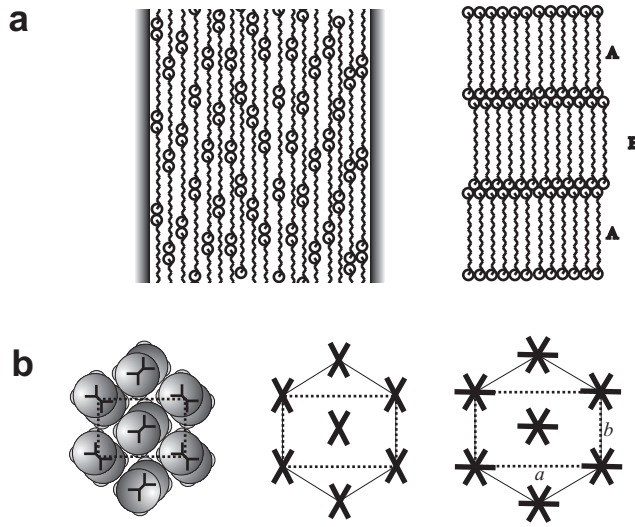


Fig. 1 – (a) A schematic side view of n-alkane  $C_{19}H_{40}$  in a nanopore and of the layered structures of the bulk phases C and  $R_I$  with a stacking scheme AB. (b) A view along the chain axis of the bulk phases C,  $R_I$ ,  $R_{II}$  (from left to right) showing the various degrees of order and disorder of the orientation of the -C-C- plane.

as a network of 3D randomly connected tubular pores with relatively uniform diameter  $d \sim 70\text{\AA}$  and average length  $l \sim 300\text{\AA}$ . The normal alkanes are one of the most basic organic series; they are the building blocks for surfactants, liquid crystals and lipids. Crystalline  $C_{19}H_{40}$  can be considered an almost rigid rod-like molecule with a length of about  $25\text{\AA}$  and a width of  $4\text{\AA}$ . The C atoms of the zig-zag backbone are all in the trans configuration, so that all of them are located in a plane. Gauche defects which lead to kinks and twists of the -C-C- chain are abundant in longer alkanes, but have little effect on the crystal structure of the phases of bulk  $C_{19}H_{40}$  [16]. In the bulk state the medium-length alkanes form layered crystals [8] (see Fig. 1). For  $C_{19}H_{40}$  the molecules are aligned perpendicular to the layers [9]. Within the layers the molecules are 2D close packed, side by side, in a quasihexagonal 2D array (Fig. 1), described by in-plane lattice parameters  $a$  and  $b$ . The azimuth of the rotation of the -C-C- plane around the long z-axis of the molecule defines an orientation. In the low-temperature phase of the bulk alkane, termed "crystalline" C, there are two different orientations which alternate in a herringbone fashion. Upon heating this phase undergoes a phase transition at 294.8 K into a state of partial orientational disorder, the so-called "rotator" phase  $R_I$  [9] [11]. Here the molecules flip between two equivalent positions. This phase melts at 304.5 K. Somewhat longer alkanes  $C_nH_{2n+2}$ ,  $21 < n < 26$ , display another mesophase with complete orientational disorder [9], the phase  $R_{II}$ , in which the molecules perform hindered rotations or flips around the z-direction between 3 equivalent orientations. This phase has a strictly hexagonal metric, that is  $a/b = \sqrt{3}$ . See Fig. 1 for the orientational pattern of the three phases C,  $R_I$ ,  $R_{II}$ . Fig. 2 shows the x-ray powder pattern of the  $R_I$  phase of the bulk solid. The dominant peaks are a series of (00l) reflections at lower Bragg angles  $2\theta$ , which are related to the layered arrangement of the molecules, and the two principal in-plane reflections around  $22\text{deg}$ . In the hexagonal lattice of phase  $R_{II}$  these two peaks would merge.

For the study of the pore condensate, the Vycor glass matrix has been soaked with the melted alkane in an evacuated glass chamber at  $T = 310\text{K}$ . Weight measurements of the glass

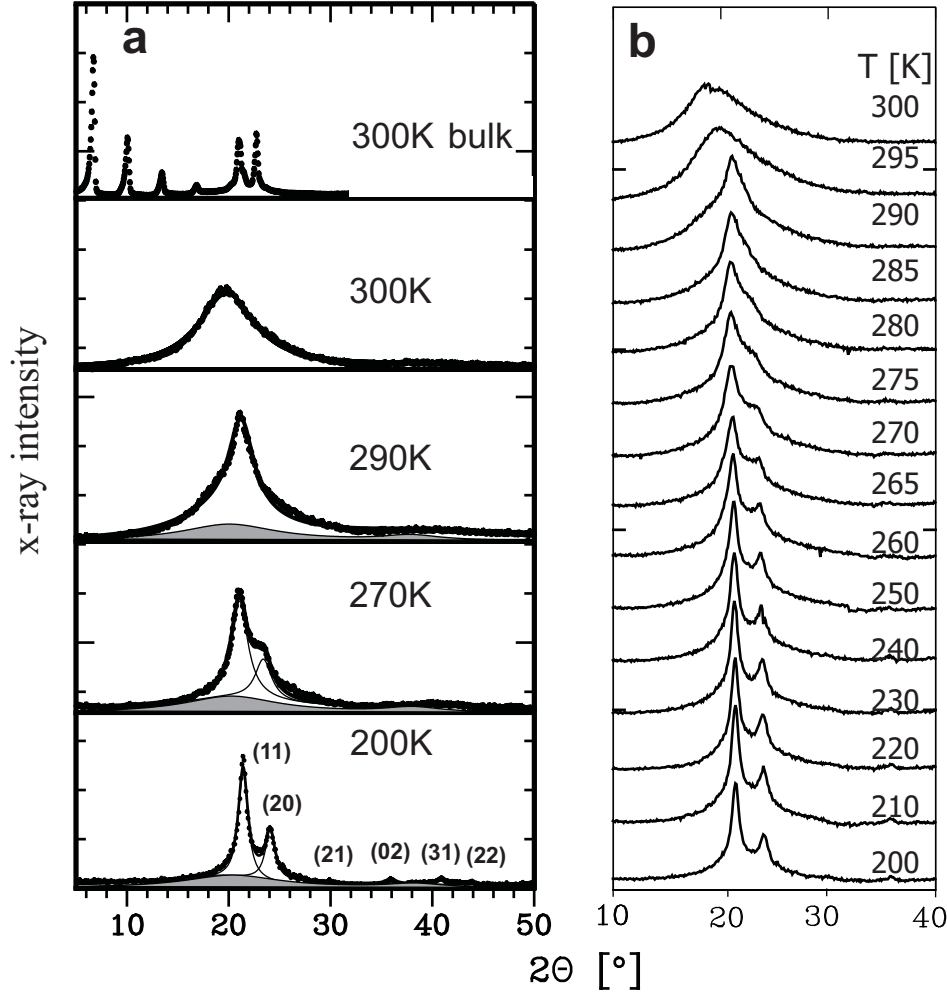


Fig. 2 – (a) Powder diffraction patterns ( $\lambda = 1.542 \text{ \AA}$ ) of the  $R_I$  phase of bulk  $C_{19}H_{40}$  (top) and of the pore condensate. The four examples shown represent the phases C and  $R_I$ , the coexistence  $R_{II}$ -liquid and the liquid state. The reflections of phase C are indexed on the basis of a two-dimensional rectangular mesh. The solid line connecting the measured intensities (circles) is the sum of the Lorentzian-type Bragg peaks plus an amorphous background (gray shaded pattern) for the confined C and  $R_I$  phase. In the case of the  $R_{II}$ -liquid state at  $T=290\text{K}$  an additional scattering component with reduced intensity but with the same overall shape as in the case of the pure confined liquid at  $T=300\text{K}$  is necessary in order to arrive at a full fit of the observed intensity. (b) Temperature dependent diffraction patterns of the confined alkane taken while heating from 200K to 300K in 5K steps.

monolith before and after filling, the known mass density of the bulk liquid, and the specific pore volume allowed us to calculate a filling fraction of  $98 \pm 2\%$  of the pores.

For an inspection of the structure of the alkane in the pores, diffraction patterns have been recorded on heating and cooling between 200 K and 310 K using a Bragg-Brentano para-focussing geometry [10]. The radiation comes from a rotating Cu anode operating at 10kW and is monochromatized by reflection from a graphite (002) crystal ( $\lambda = 1.542\text{\AA}$ ). The

diffraction patterns cover scattering angles  $2\Theta$  from  $4^\circ$  to  $50^\circ$ . The scattering background shows a broad maximum due to the first peak in the structure factor of the amorphous  $SiO_2$  matrix. This background, which amounts to about 10% at its maximum value at 22 deg, has been subtracted, properly accounting for the different x-ray absorption lengths. The resulting patterns are shown in Fig. 2. The overall appearance is totally different from the bulk reference pattern: Stronger diffracted intensity is confined to scattering angles of about 20deg. In particular the (00l) series of the bulk state has disappeared. The pattern of the confined alkane at  $T=200K$  can be derived from the bulk pattern by projecting the (hkl) Bragg peaks onto the basal plane, allowing for a slight adjustment of the in-plane lattice parameters  $a$  and  $b$ . To arrive at a full fit of the diffraction pattern, however, additional to the Bragg peaks, a broad background indicating highly disordered structures is necessary. From filling fraction dependent diffraction experiments on e.g. Ar [4] it is known that these disordered structures stem from the first few monolayers of molecules that are strongly adsorbed to the pore walls. Thus we find a partitioning of the adsorbed material into a more or less ordered and a highly disordered component. In the following we shall focus on the first, more ordered component and denote it "pore solid". The absence of any (00l) reflections in the diffraction patterns means that the pore solid is an effectively 2D arrangement of molecules with random  $z$ -coordinates, while its in-plane arrangement has changed little. Hence one basic geometric ordering principle of the bulk crystalline alkane, i.e. the layering, is suppressed.

An analysis of the coherence length  $\xi$  based on the widths of the diffraction peaks fitted with Lorentzians yields a continuous increase of  $\xi$  from about  $10\text{\AA}$  in the liquid phase to about  $\xi_{max} = 75\text{\AA}$  at  $T = 200K$  - compare Fig. 3. The saturated value  $\xi_{max}$  is close to the mean pore diameter of  $70\text{\AA}$  in Vycor; a result which can be explained only by an arrangement of the molecules' long axes parallel to the pore axis. A schematic view of the resulting structure of the pore solid in respect to the pore geometry is depicted in Fig. 1. Despite the quenched lamellar ordering, the confined alkane manages to order in a 2D close-packed arrangement. An observation which is maybe not too surprising, if one considers the analogous results on pore condensed Kr, Ar,  $N_2$ , and CO [3, 4]. These systems establish spherical close packed structures, not only in the bulk state but also in the confined state.

Does the  $T$ -evolution of the lateral arrangement in the pores have any relation to the phase sequence of the bulk system? In order to explore this question, we consult the diffraction patterns of fig. 2 and two quantities derived from these patterns after fitting the diffraction peaks with Lorentzian profiles: the area per molecule  $ab/2$  in the lateral plane and the  $a/b$  ratio. Fig. 3 shows the  $T$ -dependence of these parameters, both in the pores and in the bulk state. It is understood that one cannot expect to observe sharp phase transitions in the pores of Vycor glass. As in the case of the melting temperature mentioned above, phase transition temperatures in the pores are usually lower than those of the bulk [13]. The shift  $\Delta T = T_s^{bulk} - T_s^{pore}$  is roughly proportional to the inverse pore diameter. Therefore, the distribution of the pore diameters in Vycor glass inevitably leads to a smearing of the transition. Still, the behavior of the pore system is very similar to that of the bulk system, provided that we allow for a shift of the  $T$ -scale. The transition from phase C to the rotator phase  $R_I$  of the bulk solid is a first order transition, as the discontinuities of  $ab/2$  and  $a/b$  indicate. In the pores one observes at least clear changes of slope of the  $T$ -dependence of these parameters. Another indication that this transition actually occurs in the pores is supplied by the appearance of Bragg reflections at higher scattering angles. Due to the partial orientational disorder of the rotator phase, which implies large Debye-Waller factors, these Bragg reflections are absent in the  $T$ -range of the  $R_I$  phase. By contrast, they are clearly exhibited in the low- $T$  C phase, comp. Fig. 2,  $T=200K$ .

As can be seen in Fig. 3, the  $a/b$  ratio of the confined alkane's 2D lattice approaches and

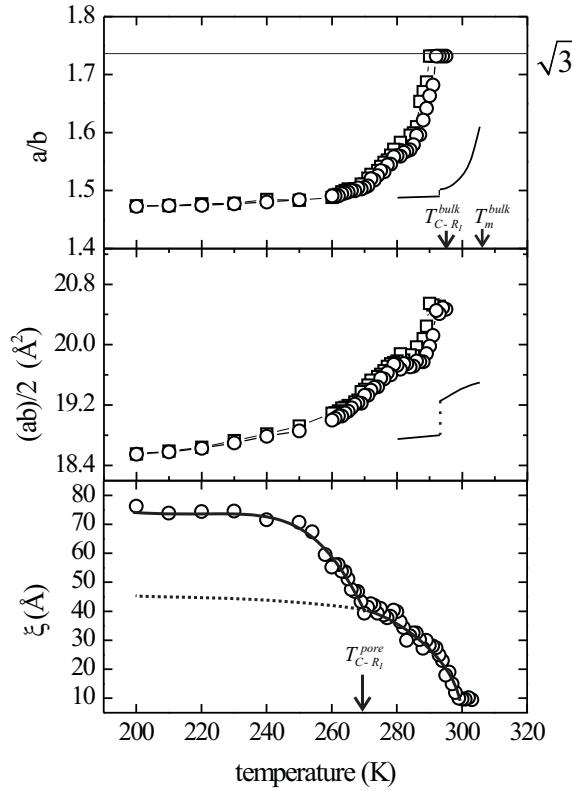


Fig. 3 – The temperature dependence of the area per molecule in the lateral plane (= pore cross section), of the ratio of the in-plane lattice parameters  $a$  and  $b$ , and of the coherence length  $\xi$  as determined from Lorentzian fits while cooling (*square*) and heating (*circ*). Results on the bulk alkane in-plane parameters ([11]) are included for comparison. The solid line in the  $(\xi, T)$ -plot is a guide for the eye. The value of  $\xi$  of the  $R_I$  phase extrapolated below  $T_{C-R_I}$  is indicated by the dashed line.

actually reaches the value of  $\sqrt{3}$ , signaling the hexagonal metric of the rotator phase  $R_{II}$ . The bulk solid, however, melts before entering this phase. Thus, the  $R_{II}$  phase is an extra feature of the pore solid. The corresponding diffraction result is the one-peak pattern at 290 K (cf. Fig. 2). This pattern can be decomposed into a sharper peak representing the  $R_{II}$  pore solid and a broader component representing the pore liquid. (A single-phase pattern of the pore liquid (at 300 K) is also shown in Fig. 2.) Obviously the pore solid melts via an intermediate state in which the liquid coexists with the  $R_{II}$  phase, although the  $R_{II}$  phase is never observed in pure form. The characteristic temperatures of the phase sequence C -  $R_I$ -mixed state  $R_{II}$ /liquid - liquid are 269 K - 289 K - 294 K on warming and 266 K - 288 K - 292 K on cooling, respectively. The uncertainty is about 1 K.

Qualitatively, the quenching of lamellar ordering can be explained in simple terms. As adsorption studies on planar and porous substrates as well as studies on liquid crystals in porous glasses have shown [14], the interaction of alkanes and other van-der-Waals systems

with the host materials is stronger than the intermolecular interaction. As monolayers, the *n*-alkanes lie flat on these substrates, side by side, their long axis and the plane of the zig-zag backbone parallel to the substrate. On a cylindrical wall, rod-like molecules will have their long axis parallel to the pore axis in order to profit most effectively from their interaction with the substrate. The pore walls of porous glasses are rough, since the matrix is an amorphous solid. On a rough wall there is a hierarchy of adsorption sites. The molecules select the deepest adsorption sites first. The positions of these sites are uncorrelated. This leads to a randomization of the *z*-coordinates of the molecules next to the walls. Obviously this positional disorder is transferred to all other molecules in the pore.

In respect to the larger *T*-width of the  $R_I$  phase as well as the appearance of the  $R_{II}$  phase, one can argue in a similar way. The orientation of the molecules next to the wall is dictated by the wall; the C-C-plane is parallel to the wall and can no longer adjust to the orientational pattern of the C or the  $R_I$  phase. The interaction with the substrates breaks not only the long-range translational order along *z*, but also the orientational order. A rough wall may furthermore induce kink defects which also destroy orientational order and are characteristic of the orientational disordered rotator phases [16]. One may speculate that the appearance of the  $R_{II}$  component owes to some part to such defects.

It is interesting to note, that complete quenching of lamellar ordering has also been reported for natural waxes, e.g. bee waxes, consisting of complicated mixtures of chain-like molecules, among them alkanes [15]. There, one attributes this phenomenon to the wide chain-length distribution, chain-branching and partially to the chemical diversity of the system.

Our findings are also reminiscent of observations in systematic studies of weakened interlayer interaction in alkanes, e.g. on chain length mixing in alkanes [12] and the induced weakening of this interaction by high pressure intercalation of inert gases between the layers [19]. Always, one observes an increased range of stability of the disordered phases, particularly of the  $R_{II}$  phase. Furthermore, in the complete absence of interlayer interaction, as in surface crystallized monolayers of alkanes floating on their own bulk liquid, only the orientational disordered hexagonal phase is observed, even in systems where this phase is not found in the bulk state, like  $C_{15}H_{32}$  [20].

A closer inspection of the *T*-dependence reveals, that  $\xi$  reaches the geometric limit dictated by the pore diameter *d* only at about  $T = 240K$ , well within the C phase. By contrast, at the  $R_I$  to C transition  $\xi$  is only  $\sim 40\text{\AA}$  and even its extrapolated value, below  $T_{C-R_I}$ , is only  $\sim 45\text{\AA}$ , indicating that the  $R_I$  as well as the  $R_{II}$  pore condensed phase is of short-range, rather than of long-range positional order. Short-range order as well as a gradual evolution of positional order are characteristic of 2D systems, 2D phase transitions resp. [17]. Along with the observed complete loss of any positional order in the *z*-direction, this encourages us to believe that the confinement leads here to a reduced dimensionality of the system, rendering it 2D-like. In fact, the  $\xi$  behavior for the confined alkane agrees with the one found for phase transitions of rod-like molecules in weakly coupled 2D layers of smectic liquid crystals, which could be described by 2D isotropic-hexatic-crystalline phase transitions [18]. Thus, we propose a mapping of the disorder-order transitions of the confined alkane on 2D models, e.g. models based on the anisotropic planar rotator as suggested for order-disorder transitions in alkane monolayers [21] or models with an XY-like primary order parameter, where this order parameter should be coupled to the zig-zag backbone orientation, and the interaction should be of a quadrupolar type. These models, enriched by external fields accounting for the random disorder introduced by the matrix should give deeper insights into the observed behavior.

In summary, the confined alkane manages to form 2D close-packed structures in the pores of Vycor despite the drastic geometric restrictions and while compromising one basic ordering principle of the bulk alkane, i.e. the lamellar ordering. Obviously the randomization of the

z-positions of the molecules does not suppress the orientational order-disorder transitions known from the bulk alkanes. On the other hand the confinement in the pores favors the disordered phases, as documented by the downward shift of the melting temperature, the appearance of the true rotator phase  $R_{II}$  and the increase in the temperature range of the partially disordered phase  $R_I$  at the expense of the crystalline phase C. As witnessed by the behavior of the coherence length of the evolving positional ordering and the observed analogies with alkanes with weakened interlayer interaction, the complete loss of any ordering along the z-direction renders the system 2D-like. Thus, the alkane confined within Vycor constitutes a fine example of how nanoconfinement leads to new structures and different phase behavior, here, in fact, to a reduction of the effective dimensionality of the system, not towards 1D, as one might have thought, but towards 2D.

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